

PATENT ABSTRACTS OF JAPAN

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(21) Application number : 08-141782 (71) Applicant : ASAHI CHEM IND CO LTD

(22) Date of filing : 04.06.1996 (72) Inventor : YAMAMOTO MIHOKO
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(54) PARTICULATE FLAME RETARDANT COMPOSITION AND FLAME-RETARDANT THERMOPLASTIC RESIN COMPOSITION

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain a particulate flame retardant composition which is easy to handle, can be blended with any thermoplastic resin, reveals a maximum effect at low loadings, and can give a flame-retardant resin with very little variation in flame retardancy and physical properties, and a flame-retardant thermoplastic resin composition made by using it.

SOLUTION: This flame retardant composition consists of at least two components which are selected from a flame retardant, a flameproofing aid and a heat stabilizer and at least one of which serves as a binder in granulation, and it satisfies the following relations: $V1=5-300\text{mm}^3$ and $S1/V1=(0.7 \text{ to } 3)$, wherein $V1$ is the volume of one particle of the composition and $S1$ is the surface area thereof. The thermoplastic resin composition is obtained by melting and kneading 100 pts.wt. thermoplastic resin with 2-45 pts.wt. of this flame retardant composition.

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TI Particulate flame retardant compositions and thermoplastic resin compositions containing them
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PA Asahi Chemical Industry Co., Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 6 pp.
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LA Japanese
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CC 37-6 (Plastics Manufacture and Processing)

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PI JP 09324071	A2	19971216	JP 1996-141782	19960604
PRAI JP 1996-141782			19960604	

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 09324071	ICM	C08K007-00
	ICS	C08L101-00

AB Title compns. comprise ≥ 2 components selected from (A) flame retardants, (B) flame retardant aids, and (C) heat stabilizers (A, B, and/or C serve as binders upon granulation) and 1 particle of the said composition has V_1 5-300 mm^3 and sp. surface areas S_1/V_1 0.7-3 (V_1 and S_1 are vols. and surface ares per 1 particle, resp.). The resin compns. are melt-kneaded products of 100 parts thermoplastic resins with 2-45 parts of the flame retardant compns. Thus, Sb2O3 3, tetrabromobisphenol A 19, and powdered polytetrafluoroethylene 0.1 part were blended and granulated to give a particulate composition having resistance to powdering. Then, the composition 22,

ABS resin 45, and acrylonitrile-styrene copolymer 55 parts were melt kneaded and molded to give a test piece showing flame retardance V-0 (UL 94).

ST flame retardant particle powdering resistant; thermoplastic resin flame retardant bromobisphenol A; antimony trioxide tetrabromobisphenol A flame retardant; heat stabilizer flame retardant thermoplastic resin

IT Fireproofing agents
Heat stabilizers

(powdering-resistant particulate flame retardant compns. for thermoplastic resins)

IT Fluoropolymers, properties

RL: MOA (Modifier or additive use); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(powdering-resistant particulate flame retardant compns. for thermoplastic resins)

IT 79-94-7, Tetrabromobisphenol A 1309-64-4, Antimony trioxide, properties 9002-84-0, Polytetrafluoroethylene

RL: MOA (Modifier or additive use); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(powdering-resistant particulate flame retardant compns. for thermoplastic resins)

IT 9003-54-7, Acrylonitrile-styrene copolymer 9003-56-9, Acrylonitrile-butadiene-styrene copolymer

RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(powdering-resistant particulate flame retardant compns. for thermoplastic resins)

DERWENT-ACC-NO: 1998-095751

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TITLE: Granulated flame retardant compsn. and flame-resistant thermoplastic resin compsn.

PATENT-ASSIGNEE: ASAHI KASEI KOGYO KK[ASAHI]

PRIORITY-DATA: 1996JP-0141782 (June 4, 1996)

PATENT-FAMILY:

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INT-CL (IPC): C08K007/00, C08L101/00

ABSTRACTED-PUB-NO: JP 09324071A

BASIC-ABSTRACT:

A granulated flame retardant compsn. (X) comprises at least two components selected from a flame retardant (A), a flame retardant assistant (B), and a heat stabilizer (C) and is granulated by using at least one component selected from (A), (B), and (C) as a binder and its particle has a volume (V1) and a surface area (S1) satisfying the following relationship: V1=5-300 cu.mm and S1/V1=0.7-3.

ADVANTAGE - (X) is easily blended with many kinds of thermoplastic resin and gives a high flame resistance to them.

CHOSEN-DRAWING: Dwg. 0/0

TITLE-TERMS: GRANULE FLAME RETARD COMPOSITION FLAME RESISTANCE THERMOPLASTIC RESIN COMPOSITION

DERWENT-CLASS: A13 A14 E14

CPI-CODES: A08-F01; E10-E02D1; E31-M; E31-P02B;

CHEMICAL-CODES:

Chemical Indexing M3 *01*

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C108 C802 C803 C804 C805 C807 M411 M782 M903 M904

Q130 Q621 R043

Markush Compounds

199809-C5001-M

Chemical Indexing M3 *02*

Fragmentation Code

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the fire-resistant thermoplastics constituent which comes to carry out melting kneading of a granular flame-retarder constituent, and thermoplastics and this granular flame-retarder constituent.

[0002]

[Description of the Prior Art] Generally, in carrying out flameproofing of the thermoplastics, it carries out initial-complement combination of a flame retarder, the fire-resistant assistant, etc., and melting kneading is carried out. At this time, it was [that a flame retarder is powdered or] liquefied in most cases.

[0003] Since dust tends to disperse at the time of combination when a flame retarder is powdered, workability is not desirable on about [being bad] and work environment. Moreover, it may become ununiformity mixing by the classification at the time of mixing with thermoplastics. When a flame retarder is liquefied, in order to raise quantum nature, a special facility of the feeder for **** etc. is needed.

[0004] As a means to cancel these faults, the flame-retarder masterbatch for thermoplastics to which the granular flame retarder which consists of a flame retarder and thermoplastics changes from the flame retarder (B) which is not fused at the resin system flame retarder (A) and this fabricating-operation temperature which are fused at the fabricating-operation temperature of the thermoplastics by which flameproofing is carried out to JP,3-22730,A is indicated by JP,4-28740,B. However, since these flame-retarder masterbatches contain thermoplastics as a binder, if the dispersibility of a flame retarder and the physical properties of a flame-retardant-resin constituent are taken into consideration, they need to choose the presentation of the thermoplastics which serves as a binder according to the resin blended, and molecular weight. Consequently, since many flame-retarder masterbatches are needed, the management will become very complicated. Moreover, in JP,55-21439,A, a halogen system compound, an inorganic flame retardant, and other inorganic system compounds are mixed with a wet method, and the technique of obtaining a granular flame retarder is indicated by performing shaping and desiccation. however -- the case where this approach cannot obtain easily the constituent which has uniform particle diameter since it is easy to carry out remelting arrival of the granular flame retarders at a desiccation process when a solvent is used on the occasion of wet blending, and it is not a solvent -- -proof -- powdering -- it becomes that in which the sex was inferior. Furthermore, the granular flame retarder containing the lubricant which has a low-melt point point rather than the inorganic flame retardant, fatty-acid amide, and fatty-acid amide which use an antimonic acid ghost as an indispensable component is indicated by JP,6-256763,A. However, in order that this granular flame retarder may contain the lubricant of a low-melt point point rather than a fatty-acid amide and it and may promote dropping of resin at the time of combustion, it is not desirable for V-UL 0 application. Moreover, the melting point of a fatty-acid amide and lubricant is low compared with the granulation temperature of thermoplastics, and it welds to the screw under a hopper in the case of a granulation, and has the fault of a lifting or a

cone for a maldistribution.

[0005]

[Problem(s) to be Solved by the Invention] As mentioned above, in the Prior art which make it easy to granulate various flame retarders and to deal with it, there was a problem of management not being complicated in order to limit the resin blended, or satisfactory physical properties and fire retardancy not being acquired since the problem was in the dispersibility of a flame retarder, or becoming the scattered thing. This invention aims at offering the fire-resistant thermoplastics constituent containing the grain flame retarder which handling can be easy, can blend with the thermoplastics of arbitration, can demonstrate the effectiveness maximum by little addition, and can give very little flame retardant resin of dispersion in fire retardancy and physical properties, and this granular-under such the actual condition flame retarder.

[0006]

[Means for Solving the Problem] this invention persons by choosing the component used as a binder from a flame retarder, a fire-resistant assistant, or the heat stabilizing agents, as a result of inquiring wholeheartedly Being restricted to the thermoplastics and the application which are blended twists, and it carries further. The shape of a grain is held under the feed hopper at the time of mixing and melting kneading, and after being transported to some extent with a screw, it crushes or fuses. A flame retarder, It came to invent the granular flame-retarder constituent which can distribute a fire-resistant assistant and a thermostabilizer to homogeneity in resin, and the fire-resistant thermoplastics constituent using this.

[0007] Namely, this invention consists of two or more components chosen from (1) flame retarder (A), the fire-resistant assistant (B), and the heat stabilizing agent (C). At least one or more components in (A), (B), and (C) serve as a binder in the case of granulation. And when the volume per one grain of granular flame-retarder constituent is set to V1 and surface area is set to S1, As opposed to the granular flame-retarder constituent characterized by for 10-1500mm of values of V1 being in the range of 3, and the value of specific surface area S1/V1 being in the range of 0.6-4, and the (2) (thermoplastics D) 100 weight section It is related with the fire-resistant thermoplastics constituent characterized by coming to carry out melting kneading of the aforementioned granular flame-retarder constituent 2 - the 45 weight sections.

[0008] The flame retarder (A) used by this invention means liquefied or the well-known compound which is a solid-state and can give fire retardancy by adding to resin in ordinary temperature, for example, the flame retarder of a halogen system and the Lynn system is mentioned. As a halogen series flame retardant, for example, an aromatic series halogenated compound, a halogenated-aromatics vinyl system polymer, Halogenation SHIANU rate resin, a halogenation polyphenyl ether, a halogenation polyphenylene thioether, An alkyl halide triazine compound etc. is mentioned. Preferably A bromine-ized bisphenol system epoxy resin, Bromine-ized bisphenol system phenoxy resin, bromine-ized bisphenol system polycarbonate resin, Bromine-ized polystyrene resin, bromine-ized bridge formation polystyrene resin, bromine-ized bisphenol SHIANU rate resin, Bromine-ized polyphenylene oxide, PORIJI bromine phenylene oxide, a deca BUROMO diphenyloxide bisphenol condensate, a TBA monomer (tetra-bromine bisphenol A), its oligomer, etc. are bromine-ized alkyl triazine compounds. As a phosphorus series flame retardant, moreover, trimethyl phosphate, triethyl phosphate, Tributyl phosphate, trioctylphosphate, TORIBUTOKISHI methyl phosphate, Triphenyl phosphate, tricresyl phosphate, TORIKUREJIRU diphosphate, Non-halogen phosphoric ester, such as octyl diphenyl phosphate, tris (chloro ethyl) phosphate, Halogen-containing acid ester, such as a screw (2, 3 dibromopropyl) 2, 3-dichloro propyl phosphate, tris (dichloro propyl) phosphate, and screw (chloropropyl) mono-octyl phosphate, etc. is mentioned. Tetra-bromine bisphenol A and its oligomer are desirable as a binder in these. These can be used combining one sort or two sorts or more.

[0009] A fire-resistant assistant (B) means the well-known compound which can give the fire retardancy which was excellent much more by using together with a flame retarder. For example, as an inorganic system fire retardancy assistant, boron system compounds, such as zirconium system compounds, such as tin system compounds, such as molybdenum compounds, such as antimony oxide, such as an

antimony trioxide, antimony tetroxide, and antimony pentoxide, molybdenum oxide, and an ammonium molybdate, tin oxide, and tin hydroxide, a zirconium dioxide, and zirconium hydroxide, boric-acid zinc, and metaboric acid barium, an iron oxide, zinc sulfide, etc. can be mentioned. This desirable is an antimony trioxide, antimony pentoxide, and molybdenum oxide. Moreover, as an organic system fire retardancy assistant, phenol novolak resin, such as phenolaldehyde novolak resin and cresol novolak resin, polytetrafluoroethylene, silicon resin, etc. are mentioned. In these, a thing desirable as a binder is polytetrafluoroethylene and is powdered polytetrafluoroethylene still more preferably. These can be used combining one sort or two sorts or more.

[0010] As a heat stabilizing agent (C), a zeolite, a hydrotalcite, a boric-acid metal salt, an ethylene-diamine-tetraacetic acid metal salt, and an organic tin system compound are mentioned. a zeolite here -- the [the Ith group of the periodic table, and] -- the [II group and] -- the zeolite which contains at least a kind of metal chosen from IV group's metal -- it is -- concrete -- a general formula (1)

Na₂O-aluminum₂O₃, SiO₂, and XH₂O (1)

(-- X shows the number of 0-6 among a formula.) -- A mold zeolite shown, Mg permutation zeolite which permuted Na of A mold zeolite with other metals, calcium permutation zeolite, Zn permutation zeolite, Sr permutation zeolite, etc. are mentioned.

[0011] As an organic tin system, dibutyltin laurate, G n-octyl SUZUJI laurate, Dibutyltin dimaleate and its copolymer, a dibutyltin screw (butyl maleate), A dibutyltin screw (octyl maleate), a G n-octyl tin screw (butyl maleate), Dibutyltin laurate maleate, a dimethyl tin screw (octylthio glycolate), A dibutyltin screw (octylthio glycolate), a G n-octyl tin screw (isoctylthioglycolate), G n-octyl tin - An S and S'-screw (iso octyl mercapto acetate) etc. is mentioned. In these, one desirable as a binder is dibutyltin dilaurate, G n-octyl SUZUJI laurate, dibutyltin laurate maleate, a G n-octyl tin screw (isoctylthioglycolate), and G n-octyl tin. - It is an S and S'-screw (iso octyl mercapto acetate). These can be used combining one sort or two sorts or more.

[0012] Although there is especially no definition as an approach of fabricating the shape of mixing and a grain of two or more components chosen from these flame retarders (A), a fire-resistant assistant (B), and a thermostabilizer (C), an approach given in JP,62-298438,A can be used, for example. In addition, the form which is said here and which was similar to a globular form, a pilaster, or it in it being granular is said. Various well-known additives, such as a pigment, a color, lubricant, an antioxidant, an ultraviolet ray absorbent, an antistatic agent, a reinforcing agent, a bulking agent, and an antimicrobial agent, can be blended with extent which does not spoil the engine performance if needed in the case of granulation. In this invention, at least one component in the - (C) component (above-mentioned [A]) is chosen from the thing used as a binder. By mixing with fine particles, even after granulating the binder in this invention, it means the component which has the role of the excipient which makes a grain shape hold in the mixture. Moreover, the above (A) which constitutes the granular flame-retarder constituent of this invention, (B), and the (C) component can completely be used at the combination and the rate of arbitration. The rate of the binder component in a granular flame-retarder constituent can be preferably used in 0.03 - 50% of range still more preferably 0.02 to 70% 0.02 to 90% by weight.

[0013] The volume per one grain of granular flame-retarder constituent is 3 5-300mm. If this is less than [5mm] three or exceeds 3 300mm, it cannot classify in the case of combination to thermoplastics, and a uniform resin constituent cannot be obtained. Moreover, the values of specific-surface-area S/V are 0.7-3. Since it classifies in case it is combination to thermoplastics as this is less than 0.7, or crushes or is hard to fuse at the time of melting kneading, a flame retarder does not distribute to homogeneity in resin. Moreover, if this exceeds 3, it will classify in the case of combination to thermoplastics, or will weld to the screw under the feed hopper at the time of melting kneading, and will not distribute to homogeneity in resin too.

[0014] As thermoplastics (D), a homopolymer, copolymers, and these rubber consolidation types are mentioned, for example. Specifically, the things which reinforced the polymer of vinyl compounds, such as polystyrene, a styrene acrylonitrile copolymer, and polymethylmethacrylate, and a copolymer, polyethylene, polypropylene, a polyphenyl ether, polyethylene terephthalate, polybutylene terephthalate, a polycarbonate, a polyamide, and these with the gum polymer, and these alloys are mentioned.

[0015] The above-mentioned thermoplastics used for this invention is fabricated by tabular [granular / desirable / and/or tabular / desirable]. In this case, when the volume per these one is set to V2 and surface area is set to S2, it is desirable that the value of 3 and specific surface area S2/V2 has 6-2500mm of values of V2 in the range of 0.45-3.

[0016] If V2 is less than [6mm] three or exceeds 3 2500mm, it will classify in the case of combination to a granular flame-retarder constituent, and will become difficult to get about the constituent of a uniform presentation. Moreover, since it classifies in case the value of S2/V2 is combination to the grain-like flame-retarder constituent which is less than 0.45, or it is hard to fuse at the time of melting kneading, it becomes difficult to get about the constituent of a uniform presentation. Moreover, if this exceeds 3, it will classify in the case of combination to a granular flame-retarder constituent, or will weld to the screw under the feed hopper at the time of melting kneading, and will become difficult to get about a too uniform constituent.

[0017] thermoplastics (D) – receiving – the addition of a granular fire retardancy constituent – 2 - 45 weight section – it is 5 - 40 weight section preferably. If the fire retardancy of the fire-resistant thermoplastics constituent obtained as they are under 2 weight sections has this insufficient and 45 weight sections are exceeded, it will become that in which shock resistance was inferior.

[0018] Although the approach of carrying out melting kneading of thermoplastics (D) and the granular flame-retarder constituent does not have especially a limit, an approach with an extruder, a Banbury mixer, a roller, etc. is mentioned, for example. Moreover, various additives, such as a flame retarder, a fire-resistant assistant, a pigment, a color, lubricant, an antioxidant, an ultraviolet ray absorbent, an antistatic agent, a reinforcing agent, a bulking agent, and an antimicrobial agent, can be then blended with extent which does not spoil the physical properties if needed. After blending other additives thermoplastics, a granular flame-retarder constituent, and if needed and mixing with a tumbler etc., it is desirable to perform melting kneading. By this actuation, the fire-resistant thermoplastics constituent which was further excellent in homogeneity can be obtained.

[0019]

[Embodiment of the Invention]

[0020]

[Example] Although an example is used for below and this invention is explained to it still more concretely, this invention does not have the range limited at all by these examples.

[0021] The manufacture antimony-trioxide (mean particle diameter: 0.79 micrometers) 3 weight section of an example granular flame-retarder constituent (1), The powder TBA monomer (tetrabromobisphenol-A mean particle diameter: 1.5 micrometers) 19 weight section, The powder polytetrafluoroethylene 0.1 weight section is put into a Henschel mixer. Under the conditions of not heating, grade mixing stirring was carried out for 3 minutes at high speed, and it was begun to carry out common powder roll die pressing, and corned under the conditions of not heating, with the granulating machine (disk dice: 2.5mm of diameters of a die hole), and 2.5mm of diameters and a cylindrical pellet with a die length of 3mm were obtained.

[0022] This pellet 30g was put into phi60mm and a cartridge container with a die length of 60mm, and the shaker performed the shaking for 2 minutes on condition that a level shaking, shaking width-of-face:40mm, and number of shakings:240 times /, and min. then, a pellet – the sieve of 22 meshes – applying – the following formula – –proof – powdering – the rate was calculated. consequently – –proof – powdering – the rate was 92.2%. Moreover, 14.7mm, the average volume per one grain of granular flame-retarder constituent was 3, and specific surface area was 1.9.

[0023] –proof – powdering – rate (%) = $W1/W0 \times 100W1$: – the granular flame retarder was obtained like the example 1 except having made into the path of 1mm, and die length of 0.7mm size of the manufacture profit **** cylindrical shape pellet of the example of weight comparison 1 granular flame-retarder constituent (2) of the pellet in front of the weight W0:shaking of the pellet which remained in the sieve. –proof – powdering – the rate was 92.0%. Moreover, 0.55mm, the average volume per one grain of granular flame-retarder constituent was 3, and surface area was 5.4.

[0024] With PCMby IEGAI [CORP.] CORP. 30 extruder (the biaxial said direction extruder, phi=

30mm, ratio-of-length-to-diameter=33), at the bottom temperature of a hopper of 150 degrees C, and the dice temperature of 240 degrees C, melting kneading was carried out and the ABS-plastics 45 weight section shown under manufacture of an example 2 flame-retardant-resin constituent, the AS resin 55 weight section, and said granular flame-retarder constituent (1) 22 weight section were corned. By dividing into three, an immediately after [melting kneading initiation] article, a medium article, and the last article, physical properties and the test piece for fire-resistant measurement were created for the pellet obtained at this time, respectively with time. The test piece for inflammable measurement performed 220 degrees C of cylinder temperatures with the cylinder temperature of 240 degrees C, and the die temperature of 45 degrees C, and the test piece for physical-properties measurement performed injection molding with the die temperature of 60 degrees C again. The following approaches estimated physical properties and flammability. The result is shown in tables 1 and 2.

[0025] In addition, molecular weight was measured in GPC and calculated by the calibration-curve method by making polystyrene into a correlation sample. The Measuring condition is as follows.

[0026]

Measuring equipment : The TOSOH [CORP.] CORP. make Column: TOSOH [CORP.] CORP. make G3000HXL, G4000HXL, G5000HXL and G6000HXL It connects with a serial. Expansion solvent : A tetrahydrofuran rate-of-flow: -- 1 ml/minABS resin: -- pellet size phi= 3mm die-length =4mm V 2= 28.3mm³ BD rubber content = 30 % of the weight AN content in the resinous principle except BD rubber = 25.8 % of the weight ** Average molecular weight Mw=11x10⁴ (PS conversion)

AS resin : pellet size phi= 2.5mm, die length = 5mm V 2=24.5mm³ AN content = 25 % of the weight Average molecular weight Mw=14x10⁴ (PS conversion)

(1) Shock resistance (IZOD impact strength)

ASTM It measured according to the approach of D-256.

[0027] (1/4 inch in a notch, test piece thickness)

(2) Bending elastic modulus ASTM It measured according to the approach of D-790.

[0028] (3) Judge inflammable UL94, the test piece thickness 1/8, 1/12 inch, and V-0 rank.

[0029] The sample was created and evaluated like the example 2 except replacing with the example of comparison 2 aforementioned granular flame-retarder constituent (1), and using said granular flame-retarder constituent (2). A result is shown in tables 1 and 2.

[0030]

[A table 1]

	開始直後品			中間品			最終品					
	IZOD		耐燃性	IZOD		耐燃性	IZOD		耐燃性	IZOD		
	(J/g)	(MPa)	1/8"	1/12"	(J/g)	(MPa)	1/8"	1/12"	(J/g)	(MPa)	1/8"	1/12"
AS	85	2830	○	○	87	2830	○	○	87	2840	○	○
AS	89	2820	○	○	88	2800	○	×	88	2820	○	×

耐燃性 : ○...V-0

...×...V-0 OUT

[0031]

[A table 2]

	物性	難燃性	均一性	総合評価
実施例2	○	○	○	○
比較例2	○	×	×	×

物 性: ○…IZODの値が 85 J/m 以上

×…IZODの値が 85 J/m 未満

難燃性: ○…開始品、中間品、最終品の1/8", 1/12"

全てV-0をクリア

×…開始品、中間品、最終品の1/8", 1/12"

いずれか1つ以上がV-0 OUT

均一性: ○…IZODの最高値と最低値の差が 5 J/m未満

×…IZODの最高値と最低値の差が 5 J/m以上

[0032]

[Effect of the Invention] clear from having explained above – as – the granular flame-retarder constituent of this invention – -proof – powdering – it can excel in a sex, and a flame retarder can distribute to homogeneity in thermoplastics, and a fire-resistant thermoplastics constituent without physical properties and fire-resistant dispersion can be given.

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] It consists of two or more components chosen from the flame retarder (A), the fire-resistant assistant (B), and the heat stabilizing agent (C). At least one or more components in (A), (B), and (C) are chosen from the thing used as a binder in the case of granulation. And the granular flame-retarder constituent characterized by for 5-300mm of values of V1 being in the range of 3, and the value of specific surface area S1/V1 being in the range of 0.7-3 when the volume per one grain of granular flame-retarder constituent is set to V1 and surface area is set to S1.

[Claim 2] The fire-resistant thermoplastics constituent characterized by coming to carry out melting kneading of the granular flame-retarder constituent 2 according to claim 1 - the 45 weight sections to the (Thermoplastics D) 100 weight section.

[Claim 3] The fire-resistant thermoplastics constituent according to claim 2 with which thermoplastics (D) will be characterized by granular and/or the value of 3 and specific surface area S2/V2 having 6-2500mm of values of V2 in the range of 0.45-3 if it is fabricated by tabular, and these volume per one is set to V2 and surface area is set to S2.

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(54)【発明の名称】粒状難燃剤組成物、及び難燃性熱可塑性樹脂組成物

(57)【要約】

【課題】取り扱いが容易で、任意の熱可塑性樹脂へ配合可能であり、少量の添加で最大限の効果を發揮し、難燃性、物性のばらつきの極めて少ない難燃性樹脂を与える事の出来る粒状難燃剤組成物、及びこれを用いた難燃性熱可塑性樹脂組成物を提供する。

【解決手段】難燃剤(A)、難燃助剤(B)、熱安定化剤(C)から選ばれた2つ以上の成分からなり、粒状化の際、(A)、(B)、(C)のうちの少なくとも1つ以上の成分はバインダーとなるものから選択され、且つ粒状難燃剤組成物1粒あたりの体積をV₁、表面積をS₁とした時、V₁の値が5～300mm³の範囲にあり、比表面積S₁/V₁の値が0.7～3の範囲にある粒状難燃剤組成物、および該粒状難燃剤組成物2～45重量部を溶融混練してなる難燃性熱可塑性樹脂組成物。

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【特許請求の範囲】

【請求項1】 難燃剤(A)、難燃助剤(B)、熱安定化剤(C)から選ばれた2つ以上の成分からなり、粒状化の際、(A)、(B)、(C)のうちの少なくとも1つ以上の成分はバインダーとなるものから選択され、且つ粒状難燃剤組成物1粒あたりの体積をV₁、表面積をS₁とした時、V₁の値が5～300mm³の範囲にあり、比表面積S₁/V₁の値が0.7～3の範囲にあることを特徴とする粒状難燃剤組成物。

【請求項2】 热可塑性樹脂(D)100重量部に対して、請求項1記載の粒状難燃剤組成物2～45重量部を溶融混練してなることを特徴とする難燃性热可塑性樹脂組成物。

【請求項3】 热可塑性樹脂(D)が、粒状及び/または板状に成形されており、これらの1つあたりの体積をV₂、表面積をS₂とすると、V₂の値が6～2500mm³、比表面積S₂/V₂の値が0.45～3の範囲にあることを特徴とする請求項2記載の難燃性热可塑性樹脂組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、粒状難燃剤組成物、及び热可塑性樹脂と該粒状難燃剤組成物とを溶融混練してなる難燃性热可塑性樹脂組成物に関する。

【0002】

【従来の技術】一般に、热可塑性樹脂を難燃化する場合には難燃剤、難燃助剤等を必要量配合し、溶融混練する。この時、難燃剤は粉末状あるいは液状である場合がほとんどであった。

【0003】難燃剤が粉末状である場合には、配合時に粉塵が飛散し易いため、作業性が悪いばかりか、作業環境上好ましくない。また、热可塑性樹脂と混合する際の分級により不均一混合になる場合がある。難燃剤が液状である場合には、定量性を上げるために液添加用フィーダー等の特別な設備を必要とする。

【0004】これらの欠点を解消する手段として、例えば、特公平4-28740号公報には、難燃剤及び热可塑性樹脂からなる粒状難燃剤が、特開平3-22730号公報には、難燃化される热可塑性樹脂の成形加工温度で溶融する樹脂系難燃剤(A)及び該成形加工温度では溶融しない難燃剤(B)から成る热可塑性樹脂用難燃剤マスター・バッチが記載されている。しかしこれらの難燃剤マスター・バッチはバインダーとして热可塑性樹脂を含有しているため、難燃剤の分散性及び難燃性樹脂組成物の物性を考慮すると、配合される樹脂に応じてバインダーとなる热可塑性樹脂の組成、分子量を選択する必要がある。その結果、多数の難燃剤マスター・バッチが必要となるため、その管理は非常に煩雑なものとなってしまう。また、特開昭5-21439号公報では、ハログン系化合物、無機系難燃剤及びその他の無機系化合物を

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湿式法にて混合し、成形、乾燥を行うことにより粒状難燃剤を得る手法を開示している。しかし、この方法は、湿式混合の際に溶剤を用いた場合には、乾燥工程で粒状難燃剤同士が再融着しやすいため均一な粒子径を持つ組成物を得られ難く、また溶剤でない場合には耐粉化性の劣ったものとなる。さらに、特開平6-256763号公報には、アンチモン酸化物を必須成分とする無機系難燃剤と脂肪酸アミド及び脂肪酸アミドよりも低融点を有する溶剤を含有する粒状難燃剤が記載されている。しかしこの粒状難燃剤は、脂肪酸アミド及びそれよりも低融点の溶剤を含有し、燃焼時、樹脂の滴下を促進するためUL規格V-0用途には好ましくない。また、脂肪酸アミド及び溶剤の融点は热可塑性樹脂の造粒温度に比べ低く、造粒の際にホッパー下のスクリューに融着して分散不良を起こしやすいという欠点を有している。

【0005】

【発明が解決しようとする課題】以上のように、各種難燃剤を粒状化して取り扱いやすくする従来の技術では、配合される樹脂を限定するため管理が煩雑であったり、難燃剤の分散性に問題があったため、満足な物性、難燃性が得られなかったり、ばらついたものになってしまいうといふ問題があった。本発明は、こうした実情の下に、取り扱いが容易で、任意の热可塑性樹脂へ配合可能であり、少量の添加で最大限の効果を發揮し、難燃性、物性のばらつきの極めて少ない難燃性樹脂を与える事の出来る粒状難燃剤および該粒状難燃剤を含む難燃性热可塑性樹脂組成物を提供することを目的とするものである。

【0006】

【課題を解決するための手段】本発明者らは、鋭意検討した結果、バインダーとなる成分を難燃剤、難燃助剤、熱安定化剤のうちのいずれかから選択することにより、配合される热可塑性樹脂及び用途に制限されることのない、さらに運搬、混合時、及び溶融混練時の供給ホッパー下では粒状を保持し、スクリューにてある程度移送された後に破碎あるいは溶融して難燃剤、難燃助剤、熱安定剤を樹脂中に均一に分散する事のできる粒状難燃剤組成物、及びこれを用いた難燃性热可塑性樹脂組成物を発明するに至った。

【0007】すなわち、本発明は、(1)難燃剤

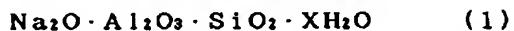
(A)、難燃助剤(B)、熱安定化剤(C)から選ばれた2つ以上の成分からなり、粒状化の際、(A)、(B)、(C)のうちの少なくとも1つ以上の成分がバインダーとなり、且つ粒状難燃剤組成物1粒あたりの体積をV₁、表面積をS₁とした時、V₁の値が10～1500mm³の範囲にあり、比表面積S₁/V₁の値が0.6～4の範囲にあることを特徴とする粒状難燃剤組成物、及び(2)热可塑性樹脂(D)100重量部に対して、前記の粒状難燃剤組成物2～45重量部を溶融混練してなることを特徴とする難燃性热可塑性樹脂組成物に関する。

【0008】本発明で使用する難燃剤(A)とは、常温で液状又は固体で、樹脂へ添加することにより難燃性を付与することの出来る公知の化合物を意味し、例えば、ハロゲン系、リン系の難燃剤が挙げられる。例えば、ハロゲン系難燃剤としては芳香族ハロゲン化合物、ハロゲン化芳香族ビニル系重合体、ハロゲン化シアヌレート樹脂、ハロゲン化ポリフェニルエーテル、ハロゲン化ポリフェニレンチオエーテル、ハロゲン化アルキルトリアルジン化合物等が挙げられ、好ましくはプロム化ビスフェノール系エポキシ樹脂、プロム化ビスフェノール系フェノキシ樹脂、プロム化ビスフェノール系ポリカーボネート樹脂、プロム化ポリスチレン樹脂、プロム化架橋ポリスチレン樹脂、プロム化ビスフェノールシアヌレート樹脂、プロム化ポリフェニレンオキサイド、ポリジプロムフェニレンオキサイド、デカプロモジフェニルオキサイドビスフェノール縮合物、TBAモノマー(テトラプロムビスフェノールA)、そのオリゴマー等、プロム化アルキルトリアルジン化合物である。また、リン系難燃剤としては、トリメチルホスフェート、トリエチルホスフェート、トリブチルホスフェート、トリオクチルホスフェート、トリブトキシメチルホスフェート、トリフェニルホスフェート、トリクレジルホスフェート、トリクレジルジホスフェート、オクチルジフェニルホスフェート等の非ハロゲンリン酸エステル、トリス(クロロエチル)ホスフェート、ビス(2,3ジプロモプロピル)2,3-ジクロロプロピルホスフェート、トリス(ジクロロプロピル)ホスフェート、ビス(クロロプロピル)モノオクチルホスフェート等、含ハロゲン酸エステル等が挙げられる。これらの中でバインダーとして好ましいのは、テトラプロムビスフェノールA及びそのオリゴマーである。これらは1種または2種以上を組み合わせて用いることが出来る。

【0009】難燃助剤(B)とは、難燃剤と併用することにより一段と優れた難燃性を付与することの出来る公知の化合物を意味する。例えば、無機系難燃助剤としては、三酸化アンチモン、四酸化アンチモン、五酸化アンチモン等の酸化アンチモン、酸化モリブデン、モリブデン酸アンモニウム等のモリブデン化合物、酸化スズ、水酸化スズ等のスズ系化合物、酸化ジルコニウム、水酸化ジルコニウム等のジルコニウム系化合物、ホウ酸亜鉛、メタホウ酸バリウム等のホウ素系化合物、酸化鉄、硫化亜鉛等を挙げることが出来る。この中で好ましいのは、三酸化アンチモン、五酸化アンチモン、酸化モリブデンである。また、有機系難燃助剤としては、フェノールアルデヒドノボラック樹脂、クレゾールノボラック樹脂等のフェノールノボラック樹脂、ポリテトラフルオロエチレン、シリコン樹脂等が挙げられる。これらの中で、バインダーとして好ましいものは、ポリテトラフルオロエチレンであり、さらに好ましくは粉末状ポリテトラフルオロエチレンである。これらは1種または2種以上を組

み合わせて用いることが出来る。

【0010】熱安定剤(C)としては、ゼオライト、ハイドロタルサイト、ホウ酸金属塩、エチレンジアミンテトラ酢酸金属塩、有機スズ系化合物が挙げられる。ここでいうゼオライトとは、周期律表第I族、第II族及び第IV族の金属から選ばれた少なくとも一種の金属を含むゼオライトであって、具体的には一般式(1)



(式中、Xは0~6の数を示す。)で示されるA型ゼオライトや、A型ゼオライトのNaを他の金属で置換したMg置換ゼオライト、Ca置換ゼオライト、Zn置換ゼオライト、Sr置換ゼオライト等が挙げられる。

【0011】有機スズ系としては、ジブチルスズラウレート、ジ-n-オクチルスズジラウレート、ジブチルスズジマレート及びその共重合体、ジブチルスズビス(ブチルマレート)、ジブチルスズビス(オクチルマレート)、ジ-ヨ-オクチルスズビス(ブチルマレート)、ジブチルスズラウレートマレート、ジメチルスズビス(オクチルチオグリコレート)、ジブチルスズビス(オクチルチオグリコレート)、ジ-ヨ-オクチルスズビス(イソオクチルチオグリコレート)、ジ-n-オクチルスズ-S, S'-ビス(イソオクチルメルカブトアセテート)等が挙げられる。これらの中で、バインダーとして好ましいのはジブチルスズジラウレート、ジ-ヨ-オクチルスズジラウレート、ジブチルスズラウレートマレート、ジ-n-オクチルスズビス(イソオクチルチオグリコレート)、ジ-ヨ-オクチルスズ-S, S'-ビス(イソオクチルメルカブトアセテート)である。これらは1種または2種以上を組み合わせて用いることが出来る。

【0012】これら難燃剤(A)、難燃助剤(B)、熱安定剤(C)から選ばれる2つ以上の成分の混合及び粒状に成形する方法としては特に限定はないが、例えば特開昭62-298438号公報記載の方法を用いることが出来る。尚、ここで言う粒状とは、球形、柱形、あるいはそれに類似した形を言う。粒状化の際、必要に応じて顎料、染料、滑剤、酸化防止剤、紫外線吸収剤、帯電防止剤、補強剤、充填剤、抗菌剤など公知の各種添加剤をその性能を損なわない程度に配合することが出来る。

本発明においては、上記(A)~(C)成分のうちの少なくとも1つの成分はバインダーとなるものから選択される。本発明におけるバインダーとは、粉体と混合することにより、粒状化した後もその混合物に粒形を保持させる賦形剤の役割を持つ成分を言う。また、本発明の粒状難燃剤組成物を構成する上記(A)、(B)、(C)成分は、全く任意の組み合わせおよび割合で使用することができる。粒状難燃剤組成物中のバインダー成分の割合は重量で0.02~90%、好ましくは0.02~7%、さらに好ましくは0.03~50%の範囲で使用することができる。

【0013】粒状難燃剤組成物1粒あたりの体積は5~300mm³である。これが5mm³未満であったり、300mm³を超えると、熱可塑性樹脂との配合の際に分級してしまい、均一な樹脂組成物を得ることが出来ない。また、比表面積S₁/Vの値は0.7~3である。これが0.7未満であると熱可塑性樹脂との配合の際に分級したり、溶融混練時に破碎あるいは溶融し難いため、難燃剤が樹脂中に均一に分散しない。また、これが3を超えると、熱可塑性樹脂との配合の際に分級したり、溶融混練時の供給ホッパー下のスクリューに融着し、やはり樹脂中に均一に分散しない。

【0014】熱可塑性樹脂(D)としては、例えば、ホモポリマー、コポリマー及びこれらのゴム強化タイプが挙げられる。具体的には、ポリスチレン、スチレン-アクリロニトリル共重合体、ポリメチルメタクリレート等のビニル化合物の重合体及び共重合体、ポリエチレン、ポリプロピレン、ポリフェニルエーテル、ポリエチレンテレフタート、ポリブチレンテレフタート、ポリカーボネート、ポリアミド及びこれらをゴム質重合体で補強したもの、及びこれらのアロイが挙げられる。

【0015】本発明に使用する上記熱可塑性樹脂は、好ましくは粒状及び/又は板状に成形される。この場合、これら1つあたりの体積をV₁、表面積をS₁とすると、V₁の値が6~2500mm³、比表面積S₁/V₁の値が0.45~3の範囲にあることが好ましい。

【0016】V₁が6mm³未満であったり、2500mm³を超えると、粒状難燃剤組成物との配合の際に分級し、均一な組成の組成物を得難くなる。またS₁/V₁の値が0.45未満であると粒状難燃剤組成物との配合の際に分級したり、溶融混練時に破碎し難いため、均一な組成の組成物を得難くなる。また、これが3を超えると、粒状難燃剤組成物との配合の際に分級したり、溶融混練時の供給ホッパー下のスクリューに融着し、やはり均一な組成物を得難くなる。

【0017】熱可塑性樹脂(D)に対して、粒状難燃性組成物の添加量は2~45重量部、好ましくは5~40重量部である。これが2重量部未満であると、得られた難燃性熱可塑性樹脂組成物の難燃性は不充分であり、45重量部を超えると、耐燃性の劣ったものとなる。

【0018】熱可塑性樹脂(D)と粒状難燃剤組成物を溶融混練する方法は、特に制限はないが、例えば、押し出し機、パンパリーミキサー、ローラー等による方法が挙げられる。また、その時必要に応じて難燃剤、難燃助剤、顔料、染料、滑剤、酸化防止剤、紫外線吸収剤、雷電防止剤、補強剤、充填剤、防腐剤など各種添加剤をその物性を損なわない程度に配合することが出来る。熱可塑性樹脂と粒状難燃剤組成物、及び必要に応じて他の添加剤を配合し、タンブラーなどでミキシングを行った後、溶融混練を行うことが好ましい。この操作により、さらに均一性に優れた難燃性熱可塑性樹脂組成物を得ることが出来る。

【0019】

【発明の実施の形態】

【0020】

【実施例】以下に実施例を用いて本発明をさらに具体的に説明するが、本発明はこれらの実施例により何らその範囲を限定されるものではない。

【0021】実施例1

粒状難燃剤組成物(1)の製造

10 三酸化アンチモン(平均粒径: 0.79μm) 3重量部、粉末TBAモノマー(テトラブロモビスフェノールA、平均粒径: 1.5μm) 19重量部、粉末ポリテトラフルオロエチレン0.1重量部をヘンシェルミキサーに入れ、非加熱条件下で高速で3分間程度混合攪拌し、一般粉末ロール型押し出し造粒機(円板ダイス: ダイス穴径2.5mm)で非加熱条件下で造粒し、径2.5mm、長さ3mmの円柱形ペレットを得た。

20 【0022】このペレット30gをΦ60mm、長さ60mmの筒形容器に入れ、振とう機にて、水平振とう、振とう幅: 40mm、振とう数: 240回/minの条件で2分間振とうを行った。その後、ペレットを22メッシュの篩にかけ、下記の式より耐粉化率を計算した。その結果、耐粉化率は92.2%であった。また、粒状難燃剤組成物1粒あたりの平均体積は14.7mm³、比表面積は1.9であった。

【0023】耐粉化率(%) = $W_1/W_0 \times 100$

W₁: 篩に残ったペレットの重量

W₀: 振とう前のペレットの重量

比較例1

30 粒状難燃剤組成物(2)の製造

得られる円柱形ペレットのサイズを径1mm、長さ0.7mmとした以外は実施例1と同様にして粒状難燃剤を得た。耐粉化率は92.0%であった。また、粒状難燃剤組成物1粒あたりの平均体積は0.55mm³、表面積は5.4であった。

【0024】実施例2

難燃性樹脂組成物の製造

下に示すAB₂S樹脂45重量部、AS樹脂55重量部、及び前記粒状難燃剤組成物(1) 22重量部を池貝

40 (株)社製PCM30押出機(2軸同方向押出機、Φ=30mm、L/D=33)で、ホッパー下温度150℃、ダイス温度240℃で溶融混練し、造粒した。この時得られたペレットを、経時的に溶融混練開始直後品、中間品、最終品の3つに分け、それぞれ物性及び難燃性測定用試験片を作成した。物性測定用試験片はシリンドーー温度240℃、金型温度45℃にて、また燃焼性測定用試験片は、シリンドーー温度220℃、金型温度60℃にて射出成形を行った。物性及び燃焼性は以下の方法で評価した。その結果を表1、2に示す。

50 【0025】尚、分子量はGPCにて測定し、ポリスチ

レンを標準サンプルとして検量線法により求めた。測定 *【0026】

条件は以下の通りである。

* 测定機器: 東ソー(株)社製

カラム: 東ソー(株)社製 G3000HXL、G4000HXL、
G5000HXL、及びG6000HXLを
直列に接続

展開溶媒: テトラヒドロフラン

流速: 1 ml/min

ABS樹脂: ベレットサイズ $\phi=3\text{ mm}$ 、長さ=4 mm、 $V_1=28.3\text{ mm}^3$

BDゴム含有量=30重量%

BDゴムを除く樹脂成分中におけるAN含有量=25.8重量%

ノ 平均分子量 $M_w=1.1 \times 10^4$ (PS換算)

AS樹脂: ベレットサイズ $\phi=2.5\text{ mm}$ 、長さ=5 mm、

$V_2=24.5\text{ mm}^3$

AN含有量=25重量%

平均分子量 $M_w=1.4 \times 10^4$ (PS換算)

(1) 耐衝撃性 (IZOD衝撃強度) ※ランクを判定する。

ASTM D-256の方法に準じて測定した。

【0029】比較例2

【0027】(ノッチ付き、試験片厚さ1/4インチ) 前記粒状難燃剤組成物(1)に代えて前記粒状難燃剤組成物(2)を用いる以外は、実施例2と同様に試料を

(2) 曲げ弾性率

20 成物(2)を使用する以外は、実施例2と同様に試料を

ASTM D-790の方法に準じて測定した。

作成、評価した。結果を表1、2に示す。

【0028】(3) 燃焼性

【0030】

UL94、試験片厚さ1/8、1/12インチ、V-0※ 【表1】

	開始品			中間品			最終品					
	IZOD		衝撃	IZOD		衝撃	IZOD		衝撃			
	(J/m)	(MPa)	1/8"	(J/m)	(MPa)	1/12"	(J/m)	(MPa)	1/8"	1/12"		
実施例2	85	2330	○	○	87	2330	○	○	87	2340	○	○
比較例2	88	2420	○	○	88	2300	○	×	88	2320	○	×

難燃性: ○…V-0

×…V-0 OUT

【0031】
【表2】

★		物性	難燃性	均一性	総合評価
		実施例2	○	○	○
	比較例2	○	×	×	×

物性: ○…IZODの値が85 J/m以上

40

×…IZODの値が85 J/m未満

難燃性: ○…開始品、中間品、最終品の1/8", 1/12"

全てV-0をクリア

×…開始品、中間品、最終品の1/8", 1/12"

いずれか1つ以上がV-0 OUT

均一性: ○…IZODの最高値と最低値の差が5 J/m未満

×…IZODの最高値と最低値の差が5 J/m以上

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【0032】

【発明の効果】以上説明してきたことから明らかなように、本発明の粒状難燃剤組成物は、耐粉化性に優れ、か

つ熱可塑性樹脂中に難燃剤が均一に分散することができ、物性、難燃性のばらつきのない難燃性熱可塑性樹脂組成物を与えることができる。

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